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Comparisons Between MM5, OM7, and Draft ASTM Measurements of Wood Stove Emissions

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ABSTRACT

The U. S. Environmental Protection Agency is developing a New Source Performance Standard (NSPS) for wood burning stoves. During the development process several issues must be resolved. One of the more critical issues is the selection of an emission sampling method and stove operating procedure. This paper addresses the comparison of three candidate sampling methods: the EPA Modified Method 5 (MM5), the Oregon Method 7 (OM7), and the ASTM proposed Method P180.

Five stoves (i.e., two catalytic, one noncatalytic generic, one noncatalytic high efficiency, and one catalytic fireplace insert) were tested. The stoves were nominally operated according to the State of Oregon's certification procedure. Simultaneous tests were conducted using MM5 and OM7 in the stove flue and MM5, OM7, and ASTM in the (ASTM) dilution tunnel. Quality assurance tests using duplicate sampling trains were also conducted. Proportional sampling, using SO_2 as a tracer gas, was conducted in the flue, and isokinetic sampling was conducted in the dilution tunnel.

Results showed good correlations between the emission measurements obtained with each method. The strength of the correlations varied with the emission format: the grams per hour format correlated the best, micrograms per Joule heat output second, and grams per kilogram dry wood burned the weakest. POM emissions showed a general correlation with total emissions but only when the grams per hour format was used; the correlations were very weak to nonexistent when the emissions were expressed in either of the other two formats.

INTRODUCTION

The U. S. Environmental Protection Agency (EPA) recently announced(1) its intent to develop a New Source Performance Standard (NSPS) for the residential wood combustion source category. The Agency discussed numerous aspects of the planned standards development program. One of the key technical decisions is the selection of a procedure for measuring wood stove emissions. This paper addresses a project which compared three wood stove emission measurement procedures: EPA Modified Method 5(2), Oregon Method 7(3), and the proposed ASTM Method P180(4). The first two methods typically collect an emission sample directly from the stack. The third method requires dilution of the entire stack flow with ambient air; a sample of the emissions is then collected from the diluted gas stream. In this project simultaneous samples were collected by MM5 and OM7 in the stack and by all three procedures from the dilution tunnel. Emission samples were collected from five stoves operated over a range of burnrates. Sample analyses followed published procedures for each of the three sampling methods. In addition, the MM5 samples were analyzed for phenol and selected polynuclear organic materials (POMs). The following sections discuss stove operation, and sampling and analysis procedures, and summarize the data obtained. Comparisons are drawn between the results obtained by the procedures evaluated.

EXPERIMENTAL METHODS

Stoves and Stove Operation

Five appliances were tested: two catalytic free standing stoves (Blaze King - King Model KEJ 1101 and TimberEze Model 477), one catalytic fireplace insert (Fisher Tech IV), one advanced design noncatalytic stove (BOSCA Model FS-500), and one conventional noncatalytic stove (Lakewood Model Cottager).

The test installation is depicted in Figure 1. The stove under test was placed on a scale to provide a burnrate record; the water seal allowed the stove free vertical movement as the weight of the wood charged decreased during a burn. In general, stove operation followed the State of Oregon and the proposed ASTM procedures; when in conflict, the Oregon procedure took precedent.

Test fuel consisted of air dried Douglas fir dimension lumber. Fuel charges were assembled according to Oregon procedures. The moisture content of each piece was determined with a Delmhorst Model G-30 electrical conductivity meter. The higher heating value for each test charge was determined by bomb calorimeter on a composite sawdust sample collected as the lumber was cut.

Emission Measurement

Five sampling trains were in operation during every test burn. In addition, most burns included one or more duplicate trains for QA purposes. Each of the three procedures is discussed separately in the following paragraphs. MM5 and OM7 procedures were the same whether the trains were operated in the stack or in the dilution tunnel.

Modified Method 5 (MM5).

The MM5 sampling train was developed for use on sources which emit organic compounds[2]. The principal modification consists of a heat exchanger and a jacketed glass module containing an organic adsorbent resin (XAD-2) between the filter holder and first impinger. The sample is cooled as it passes through the indirect heat exchanger located ahead of the XAD-2 module. The XAD-2 module is cooled by circulating ice water through the jacket. Moisture condensing in the sample line flows through the XAD-2 resin and collects in the condensate (first) impinger.

An additional probe and front filter housing rinse was performed with methanol on the MM5 trains from the burns on the BOSCA and Fisher stoves. These rinses were not included in the final results.

Analysis of MM5 samples proceeded as depicted in the block diagram of Figure 2. POM analysis was performed (by GC/MS) on an aliquot of the complete sample for each burn.

Oregon Method 7 (OM7).

OM7 is the procedure specified by the State of Oregon for all State wood stove certification tests[3]. The sampling train used is similar to MM5 except that there is no XAD-2 module. Additionally, a second, unheated filter is placed between the third and fourth impingers. Front- and back-half rinses with dichloromethane were added to the Oregon procedure for these tests.

Analysis of OM7 samples is depicted in Figure 3. The dichloromethane and acetone front-half rinses were combined before analysis; whereas, the back-half acetone rinse was analyzed separately from the combined impinger water and dichloromethane rinse.

Proposed ASTM P180.

The proposed ASTM procedure consists of a dilution tunnel to precondition the flue gases and the sampling train[4]. The dilution tunnel accepts the entire stack gas flow, diluting it with ambient air in the ratio of 45.4 to 181.6 kg air per kg of wood burned. The sampling train consists of an unheated probe and back-to-back unheated filters. An advantage of this procedure is that one can make a direct flow measurement in the tunnel, thus avoiding potential errors in the indirect calculation of flow as might arise in the Oregon procedure. On the other hand, relatively small filter net weights and the use of filters as the only collection media may be disadvantages.

Impingers were added to the ASTM train for these tests to provide a direct measure of the diluted gas moisture content. Sample analysis is shown schematically in Figure 4. The dichloromethane rinse was analyzed separately from the combined acetone/methanol rinse. Each of the filters from a test burn was analyzed separately.

Continuous Emission Monitors

CO, CO_2, and O_2 were measured and recorded continuously throughout each burn; CO and CO_2 by an Anarad Model AR-412, and O_2 by an MSA Model 820p. Each instrument was calibrated before and after each burn; zero and span checks were made every 2-3 hours during each burn. A continuous sample of the stack gas was extracted at the same height as the MM5/OM7 sampling ports. The sample passed through a conditioning system which included an ice trap and in-line filter to remove particles and heavier organics prior to introduction into the analyzers. The output from each analyzer was recorded on a Solter Model 1243 strip chart recorder. Five-minute average CO, CO_2, and O_2 values were calculated from the strip chart trace for input into the Oregon stack loss model used to calculate stack flowrate.

In addition, 1-hour average CO, CO_2, and O_2 concentrations were determined using Orsat analyses of integrated bag samples. SO_2, used as a tracer gas to determine changes in stack flow, was injected immediately above the stack sampling station. A sample of stack gas was extracted approximately 1.5 m above the injection point for SO_2 analysis.

RESULTS

A project of this complexity generates a large body of data worthy of a many faceted analysis. Of necessity, the following discussion is limited to a summary of the two major study objectives: (1) the relationships between the total emission rates as determined by the various emission measurement methods, and (2) the relationships between total emission rates as measured by the various methods and POM emission rates determined from the MM5 stack and dilution samples. Embedded within this is an analysis of the effect the units (format) used to express emission rates have on the method-to-method and method-POM relationships.

Comparison of Total Emission Measurements

A total of 20 test burns were completed. Emission results are presented in Table I in the grams per hour format. Burnrate and heat output are also included which allows the calculation of emissions in grams per kilogram of dry wood burned and micrograms per Joule heat output. Test burn numbers ending in "Q" present the results for the duplicate trains, run during the non-Q suffix burns, for QA purposes.

EPA has published procedures[5,6] for calculating stack gas flow on combustion equipment from measured values of CO, CO_2, O_2, and moisture concentrations in the stack, and the fuel composition. This method relates the CO, CO_2, and O_2 through the use of F-factors which are derived from stoichiometric combustion of a given fuel. The F-factor equation is:

$$\text{F-factor} = \frac{20.9 - (\%O_2 - 0.5\%CO)}{\%CO_2 + \%CO} = 1.000 - 1.120 \text{ for wood}$$

When this equation was applied to the data from the continuous emission monitors (CEMs), only burn numbers 5B, 4H, 5H, and 3F fell within the desired F-factor range. Orsat data derived F-factors fell within the range on nine burns (1T, 2T, 1B, 2B, 1G, 2G, 4G, 4H, and 2F). F-factors calculated from wood stove certification data submitted by the State of Oregon to EPA fell within the expected range on virtually every test. Based on this and the fact that the F-factor approach is widely applied and accepted for other combustion sources, it was decided to use it as the criterion for selecting the results (CEMs or Orsat based) reported in Table I. For those burns where neither the CEMs nor the Orsat data produced an F-factor in the desired range, the data set giving a value nearer to the desired range was reported. Burns in this category were [burn No. (F-factor)]: 4B (1.150), 3G (1.123), 1H (1.127), 2H (1.310), 2F (1.155), and 4F (1.176). For burns 3B and 3H only Orsat data were available; F-factors for these burns were 1.150 and 1.176, respectively. The data presented in Table I are thus a combination of CEMs and Orsat based results. Burns 5B, 2H, 5H, 3F, and 4F are CEMs based using the Oregon stack loss procedure to calculate stack flow. All remaining results are Orsat based using the EPA stack flow calculation procedure[6].

The preceding discussion leaves unanswered the question of why the CEMs data, in particular, were apparently in error. In summary there seem to be two principal sources of error. First, the F-factor is very sensitive to small instrument variations within the normal ± 2 percent accuracy range. This variability alone could shift the F-factor outside the desired range. The second potential source of error is the O_2 instrument used for these tests which utilizes a zirconium oxide detector operating at 760°C. At this condition reactions were likely between the gaseous components which would have resulted in faulty O_2 readings. This interference would not have been detected using normal calibration procedures. Unfortunately, this potential interference was not brought to light until all sampling was completed.

Significant deviations from the established stove operating procedure occurred during the two test burns on the TimberEze stove. During both test burns it was necessary to briefly open the stove doors 3 or 4 times to prevent the fire from dying. This deviation was deemed acceptable in light of the objectives of the project. During four test burns (1T, 3B, 4B, 2H) the fire died before all fuel was consumed; remaining fuel weights were 0.27, 13, 0.27, and 0.32 kg, respectively. Test burn 3H was terminated due to loss of electrical power before all fuel was burned. The heat output results for burns 3B and 3H were estimated from the heat input for the burn and the average overall thermal efficiency for the other burns on the respective stove since the burn did not proceed far enough to enable an accurate heat balance calculation. In addition to these deviations, there were occasional miscellaneous problems such as temporary power loss to some of the sampling systems due to circuit overloads (1T and 1G) and temporary loss of an OM7 filter heater in the dilution tunnel (5B).

Due to the above deviations/problems, the results obtained here may not be comparable to certification data published by the State of Oregon. Nevertheless, these results are felt to be adequate to achieve the stated objectives of this program.

Linear regression analyses were performed on many combinations; the ones reported here are those based on MM5 as the referee or predictor (x) variable. The resulting relationships are summarized in Table II which notes the slope, y intercept, and correlation coefficient (r^2) values. A typical case is shown in Figure 5. The strength of the correlations was quite variable. As a general rule, the strongest correlations appeared when emissions were reported in the g/hr format and weakest for the g/kg format. Correlations between the stack and dilution tunnel measurements were much weaker than stack-to-stack and dilution tunnel-to-dilution tunnel correlations. Some of the scatter may be attributable to the deviations/problems noted above. In particular there remains some doubt as to the accuracy of the stack flow calculation due to the aforementioned suspected inaccuracy in the stack gas concentration measurements.

Combining MM5 stack - OM7 stack results in Table I with those reported earlier[7] produces a data base consisting of 29 test burns. The additional nine burns consist of seven on a catalytic stove and two on a conventional noncatalytic stove. Linear regressions performed on this combined data base produced the following result:

$$OM7_s = 0.596(MM5_s) + 0.3, \text{ g/hr} \quad (r^2 = 0.90)$$

These results, based on a 50 percent larger data base, should be used in preference to the Table II values for comparing MM5 to OM7.

MM5 in the stack did not correlate 1:1 with MM5 in the dilution tunnel. As noted in Table II, $MM5_s$ was larger than $MM5_d$. Two possible reasons are: (1) inaccuracies in stack or dilution tunnel flowrate measurement, and (2) condensation of organics onto the stack and dilution tunnel walls. Errors in flow measurement cannot be ruled out, as noted previously.

The second potential reason for the lack of a 1:1 correlation is condensation of organics onto the stack and dilution tunnel walls between the respective sampling stations. As tested there was approximately 2.1 m of insulated stack and 7.6 m of uninsulated dilution tunnel between sampling stations. The stack and dilution tunnel walls, which were not cleaned between tests, had a noticeable coating by the end of the program. A comparison of the ratio of semivolatile (TCO) to condensible (GRAV) material in the dilution tunnel samples versus the stack samples showed that the ratio of $(TCO/GRAV)_d$ to $(TCO/GRAV)_s$ ranged from 0.99 to 2.76 with a mean of 1.17. This indicates that condensation onto the walls reduced the average molecular weight of organics present in the dilution tunnel compared to the stack as the heavier compounds would tend to condense more readily. Particularly with the dilution tunnel and its relatively cool, large internal surface area, condensed material from prior tests may also have influenced the results from subsequent tests, an effect which has been previously documented[7].

Correlation of POM and Total Emissions

The second major objective of this project was to look for correlations between the rate of emission of POMs and total emissions. Twenty-one POM compounds (See Table III) were selected as surrogates for the

whole compound class. It was reasoned that variations in the sum of these 21 would reflect variations in the whole class.

The POM analysis was performed by GC/MS on aliquots of each MM5 sample as noted in Figure 2. POM analyses were not performed on samples from the other methods. The results of linear regression analyses of POM emission rates versus total emission rates are presented in Table IV.

The initial conclusion drawn from Table IV is that the sum of the 21 POMs correlates with total emissions if the emissions are expressed in g/hr. There is no apparent correlation using either g/kg or ℓ g/J formats. A closer look at the g/hr correlation (Figure 6) indicates that it is strongly dependent on one high emission burn (4G). A second set of linear regressions, run with this point removed, resulted in stronger correlations for both the stack and dilution tunnel data sets but with much smaller slopes. The slope, intercept, and r^2 values are: 0.0242, 0.2, 0.95 (stack), and 0.025, -0.33, 0.91 (dilution), respectively.

Separate regressions were also run for the catalytic and noncatalytic stoves on the stack and dilution tunnel data sets. As shown in Table IV fairly strong correlations appear to exist only for the noncatalytic stoves. These results are presented graphically in Figures 7 and 8. In this case eliminating the high emission point (4G) gave a no-correlation result for the noncatalytic stoves both in the stack and in the dilution tunnel. Attempts to find correlations by stove type for the g/kg and ℓg/J formats failed for both stack and dilution data sets.

It appears that there may be a general correlation between total emissions and POMs only when the emissions are expressed in g/hr. This correlation may exist only for noncatalytic stoves; however, the current data base is too small to justify a firm conclusion. Although the catalytic stoves tested did not show any correlation between total emissions and POMs, it is very apparent that as a class the catalytics emitted POMs at much lower rates than did the noncatalytics tested. It is possible that the actual relationship (if one exists) between MM5 emissions and POMs is nonlinear. At low MM5 emission rates the curve may have a slope in the 0.02 - 0.03 range, increasing toward 0.1 at very high burnrates.

SUMMARY AND CONCLUSIONS

Wood stove emissions were sampled simultaneously in the stack by EPA MM5 and Oregon M7 and in the dilution tunnel by MM5, OM7, and proposed ASTM. Five stoves were tested, three catalytic and two noncatalytic. Linear regression analyses on total emissions as collected by each method produced from strong to very weak correlations between methods. The strongest correlations occurred when the emissions were expressed in g/hr; ℓg/J output and g/kg dry wood burned ranked second and third, respectively. In general, stack-to-stack and dilution tunnel-to-dilution tunnel correlations were significantly stronger than the cross correlations. Based on the sum of the 21 POM compounds quantified, POMs generally correlated with total emissions but only when the emissions were expressed in g/hr; no correlations were found for either ℓg/J or g/kg. The catalytic stoves tested had significantly lower POM emission rates compared to the noncatalytic stoves tested.

ENDNOTES

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Table I. Summary of Emission Results in Grams Per Hour

Burn Number	Stove Name	Burn Rate (kg/hr)	Heat Output (MJ/hr)	Stack Emissions MM5	Stack Emissions OM7	Dilution Tunnel Emissions MM5	Dilution Tunnel Emissions OM7	Dilution Tunnel Emissions ASTM	POM Emissions Stack	POM Emissions Dil.Tun.
				--Grams--Per--Hour----		----Grams--------Per----------			----Hour--	
1T	Timber-Eze	0.9	11.36	17.010	8.010	11.340	6.156	4.257	0.097	0.082
2T	Timber-Eze	1.22	15.83	14.640	7.552	13.298	4.892	3.367	0.081	0.038
2TQ	Timber-Eze	1.22	15.83					0.998		
1B	Blaze King	1.09	11.80	7.129	4.589	10.900	4.153	2.300	0.035	0.038
1BQ	Blaze King	1.09	11.80		4.164			2.344		
2B	Blaze King	2.77	33.94	20.830	10.803	24.154	10.709	8.559	0.139	0.176
2BQ	Blaze King	2.77	33.94		10.221					
3B(1)	Blaze King	0.34	4.28	5.440	2.496	15.844	9.418	2.910	0.032	0.040
4B	Blaze King	0.6	6.62	23.100	7.980	10.680	7.980	4.500	0.020	0.047
4BQ	Blaze King	0.6	7.62				3.966			
5B(2)	Blaze King	1.64	23.51	9.758	3.001	13.399	9.282	4.969	0.082	0.073
5BQ	Blaze King	1.64	23.51	8.495		15.268			0.080	0.079
1G	Lakewood	0.89	10.35	54.646	29.192	54.023	24.365	27.269	0.149	0.186
2G	Lakewood	1.51	17.50	45.300	26.878	54.511	28.388	22.046	0.337	0.492
3G	Lakewood	1.17	14.01	56.394	32.175	74.763	27.027	33.696	0.228	0.535
3BQ	Lakewood	1.17	14.01		35.100	53.235				0.503
4G	Lakewood	7.17	101.78	216.534	61.304	179.929	54.564	96.795	19.287	12.763
4GQ	Lakewood	7.17	101.78	216.534			88.908		16.921	
1H	BOSCA	1.46	20.54	12.571	9.388	32.704	10.658	9.855	0.508	0.791
1HQ	BOSCA	1.46	20.58		7.096			8.760		
2H(2)	BOSCA	0.54	8.41	30.456	21.222	18.522	8.262	12.150	0.092	0.034
2HQ	BOSCA	0.54	8.41				12.798			
3H(1)	BOSCA	0.6	8.27	17.220	6.960	56.400	20.220	19.680	0.476	1.056
3HQ	BOSCA	0.6	8.27	16.740		59.580			0.252	1.470
4H	BOSCA	1.08	14.77	14.688	8.488	28.512	8.662	9.104	0.395	0.386
5H(2)	BOSCA	3.1	42.82	50.220	25.947	68.200	37.200	20.429	4.495	4.557
1F	Fisher	2.02	30.83	38.784	29.088	71.508	36.966	30.300	0.149	0.146
2F	Fisher	0.55	9.23	8.525	4.626	22.550	10.725	4.169	0.017	0.037
2FQ	Fisher	0.55	9.23			14.905				0.022
3F(2)	Fisher	1.58	24.87	19.592	15.958	48.032	21.330	13.351	0.083	0.124
4F(2)	Fisher	0.95	15.06	17.290	20.330	23.940	13.018	6.242	0.045	0.025
4FQ	Fisher	0.95	15.06			28.310				0.032

(1) Incomplete burn; stack data suspect.
(2) Stack flow calculated from continuous emission monitor CO, CO_2, O_2 values. Orsat data used for all other burns.

Table II. Linear Regression Results for Total Emissions

Dependent (y) Variable		Slope	y-Intercept	r^2
		(1) $MM5_s$ = Independent (x) Variable		
$OM7_s$ (2)	g/hr	0.580	2.04	0.87
	g/kg	0.555	0.16	0.81
	µg/J	0.536	0.03	0.84
$MM5_d$ (3)	g/hr	0.755	13.52	0.88
	g/kg	0.639	11.60	0.55
	µg/J	0.729	0.69	0.67
$OM7_d$ (3) (2)	g/hr	0.537	1.98	0.67
	g/kg	0.323	5.28	0.61
	µg/J	0.349	0.33	0.72
ASTM (3) (2)	g/hr	0.555	-1.74	0.82
	g/kg	0.453	0.11	0.80
	µg/J	0.472	-0.03	0.83
		$MM5_d$ = Independent (x) Variable		
$MM5_s$ (3)	g/hr	1.167	-11.45	0.88
	g/kg	0.867	0.321	0.55
	µg/J	0.921	-0.06	0.67
$OM7_s$ (3) (2)	g/hr	0.407	1.97	0.74
	g/kg	0.556	-1.10	0.60
	µg/J	0.548	-0.07	0.71
$OM7_d$ (2)	g/hr	0.465	0.02	0.91
	g/kg	0.386	2.36	0.87
	µg/J	0.394	0.15	0.89
ASTM (2)	g/hr	0.430	-2.05	0.86
	g/kg	0.397	-0.68	0.77
	µg/J	0.416	-0.09	0.80

(1) Subscripts: s = stack, d = dilution tunnel.
(2) Burn 4G omitted from these g/hr correlations.
(3) Burns 3B and 3H omitted from stack-dilution tunnel cross correlations.

Table III. Target POM Compounds for Quantitative GC/MS Analysis

acenaphthene	indeno(1,2,3,-cd)pyrene
anthracene	naphthalene
benzo(a)anthracene	phenanthrene
benzo(a)pyrene	pyrene
benzo(b)fluoranthene	1-nitronaphthalene
benzo(g,h,i,)perylene	9-methylcholanthrene
benzo(k)fluoranthene	carbazole
chrysene	acridine
dibenzo(a,h)anthracene	9-phenanthrol
fluoranthene	pyrenequinone
fluorene	

Table IV. Linear Regression Results for POMs vs MM5 Total Emissions

MM5 Emissions = Independent (x) Variable
All Stoves, All Data Points

POM Emission = Dependent (y) Variable (1) (2)	Slope	y-Intercept	r^2
$MM5_s$ g/hr	0.0838	-1.6	0.89
vs g/kg	0.00308	0.26	0.0069
POM_s µg/J	0.00207	0.021	0.0041
$MM5_d$ g/hr (2)	0.0691	-1.7	0.76
vs g/kg	0.0139	-0.03	0.23
POM_d µg/J	0.0125	0.00053	0.22

Catalytic Only

	Slope	y-Intercept	r^2
$MM5_s$ g/hr	0.00314	0.0190	0.43
$MM5_d$ g/hr	0.00168	0.035	0.39

Noncatalytic Only

	Slope	y-Intercept	r^2
$MM5_s$ g/hr (2)	0.0896	-2.2	0.90
$MM5_d$ g/hr (2)	0.0881	0.035	0.88

(1) Subscripts: s = stack; d = dilution tunnel
(2) This result is strongly influenced by Burn No. 4G

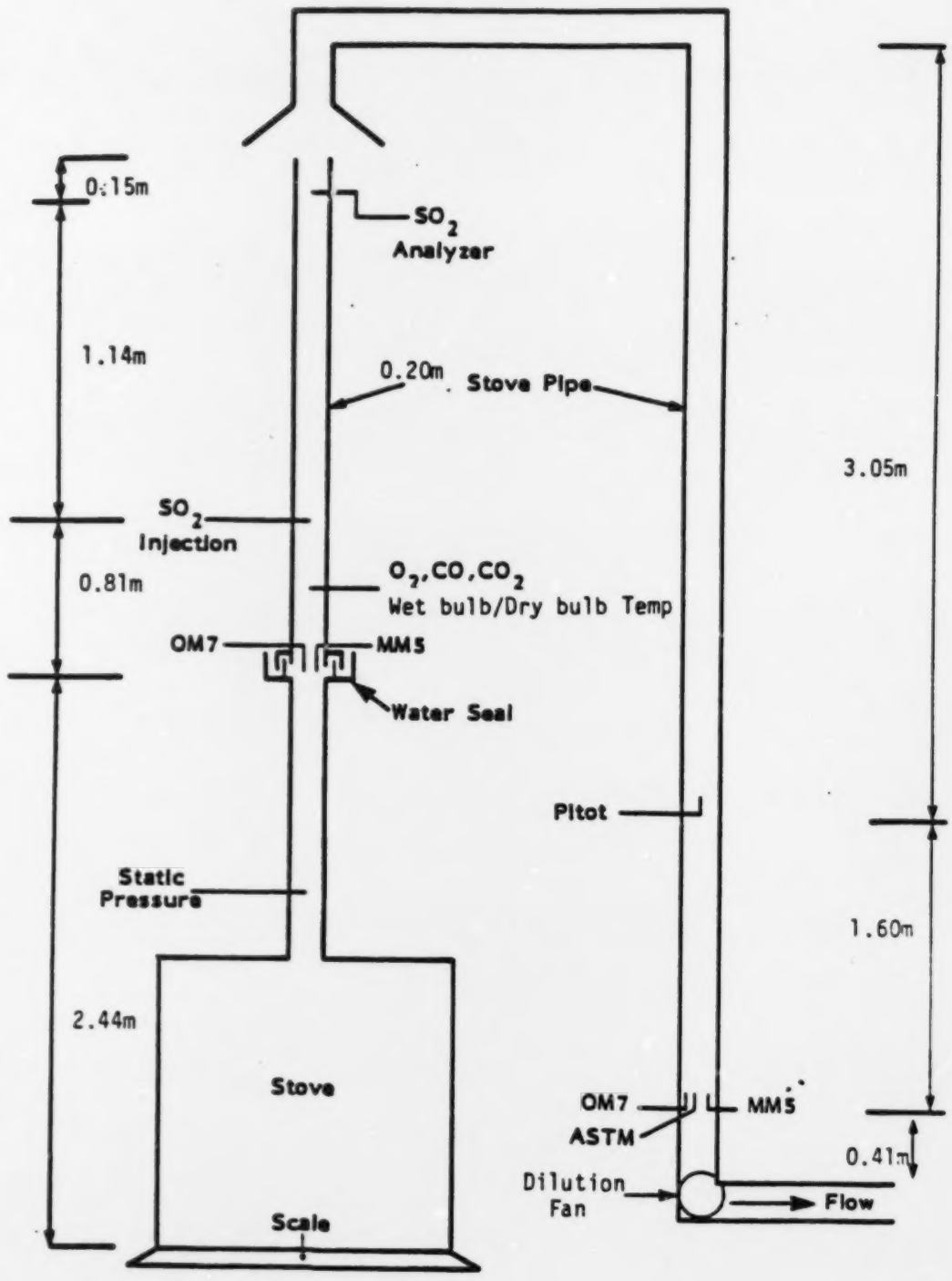

Figure 1. Schematic of stove exhaust and dilution system with sample locations.

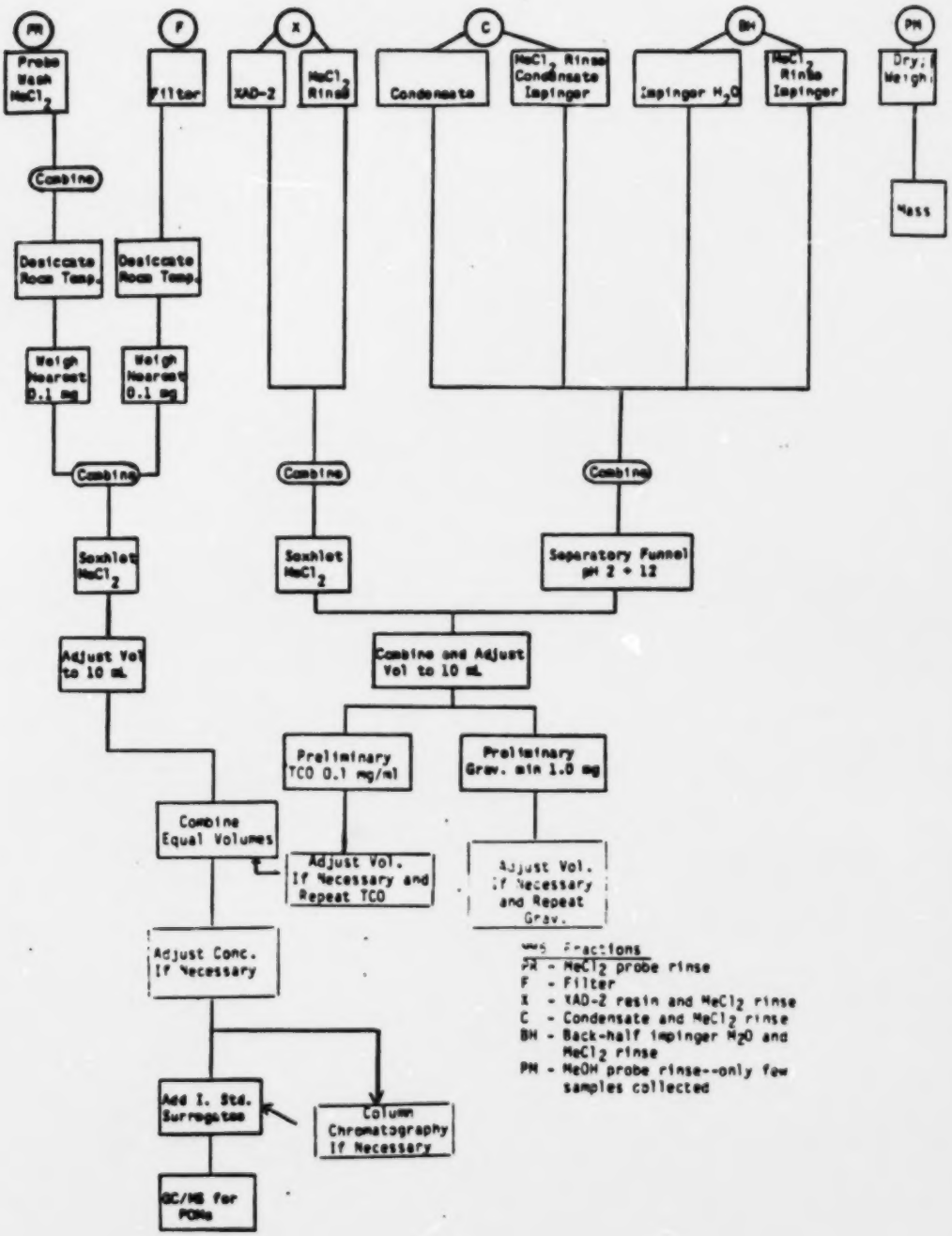

Figure 2. EPA 23 sample fractions and analytical matrix.

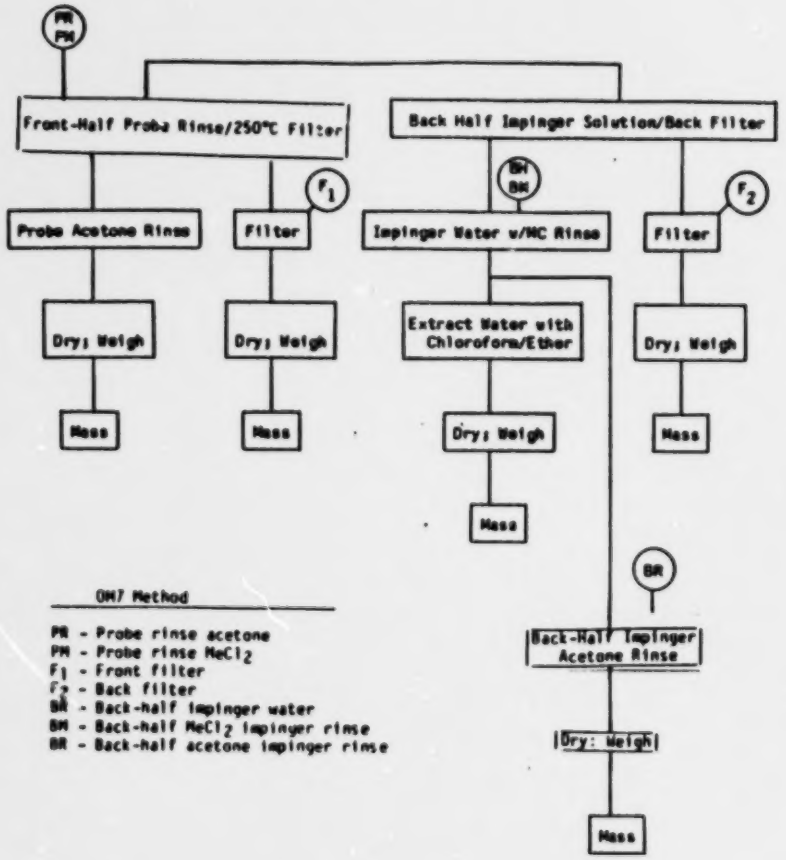

Figure 3. Oregon Method 7 sample fractions and analytical matrix.

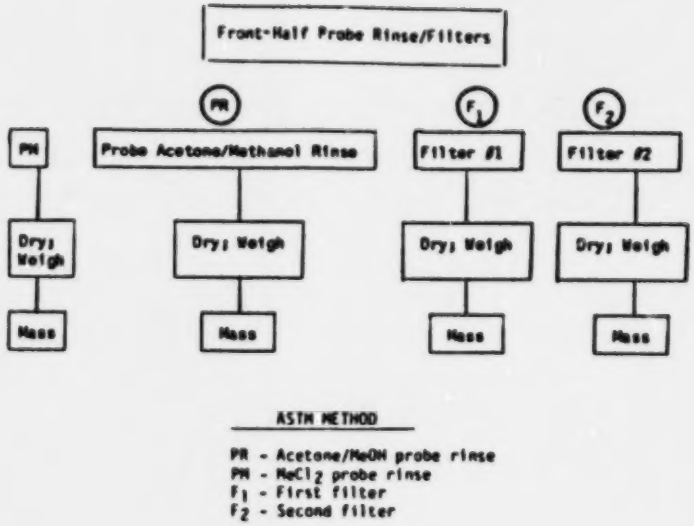

Figure 4. ASTM sample fractions and analytical matrix.

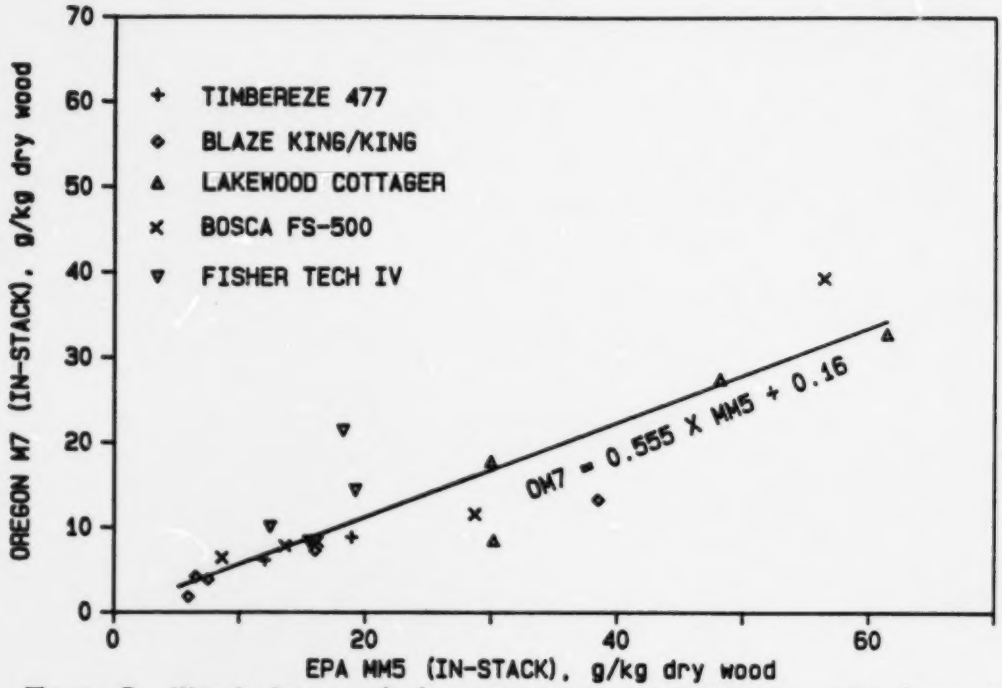

Figure 5. Wood stove emission measurement methods comparison of OM7 vs MM5 in-stack in grams per kilogram of dry wood burned.

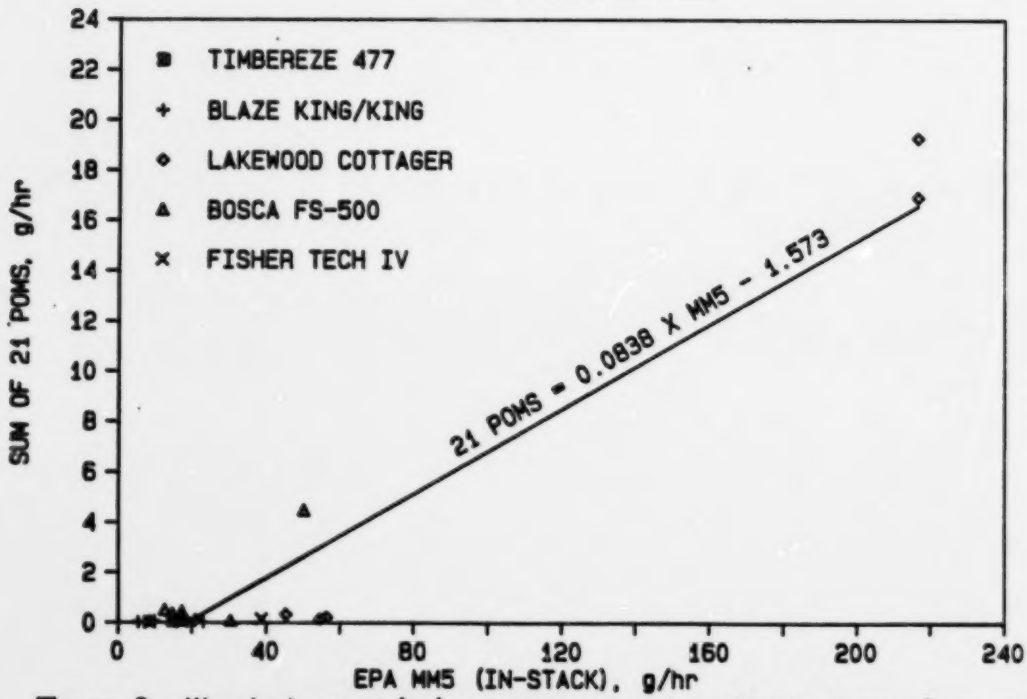

Figure 6. Wood stove emission measurement methods comparison of the sum of 21 POMs vs MM5 in-stack in grams per hour.

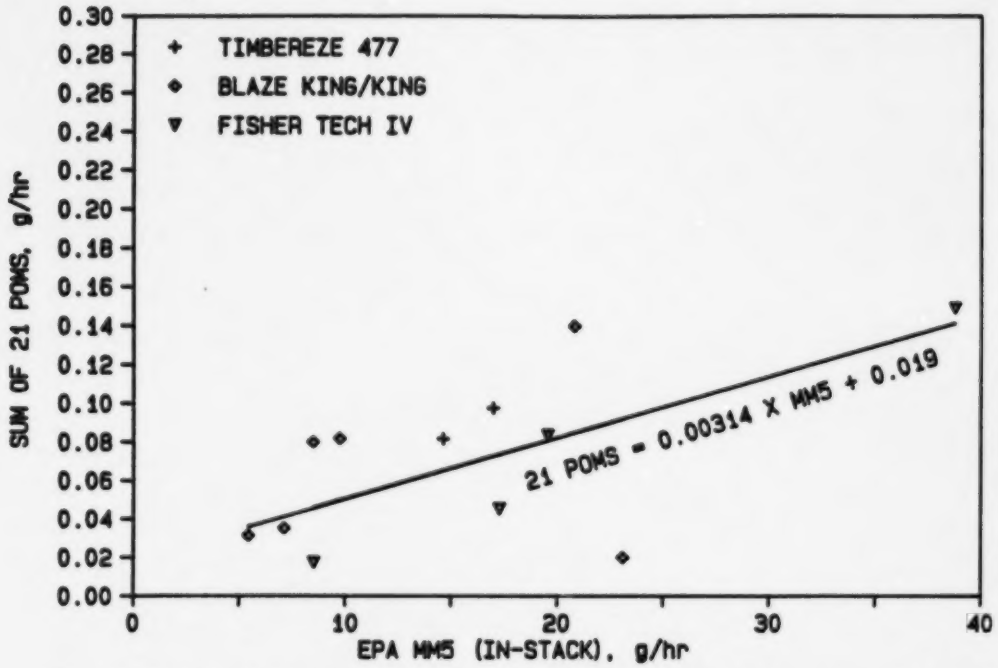

Figure 7. Wood stove emission measurement methods comparison of sum of 21 POMs vs MM5 in-stack in grams per hour for catalytic stoves.

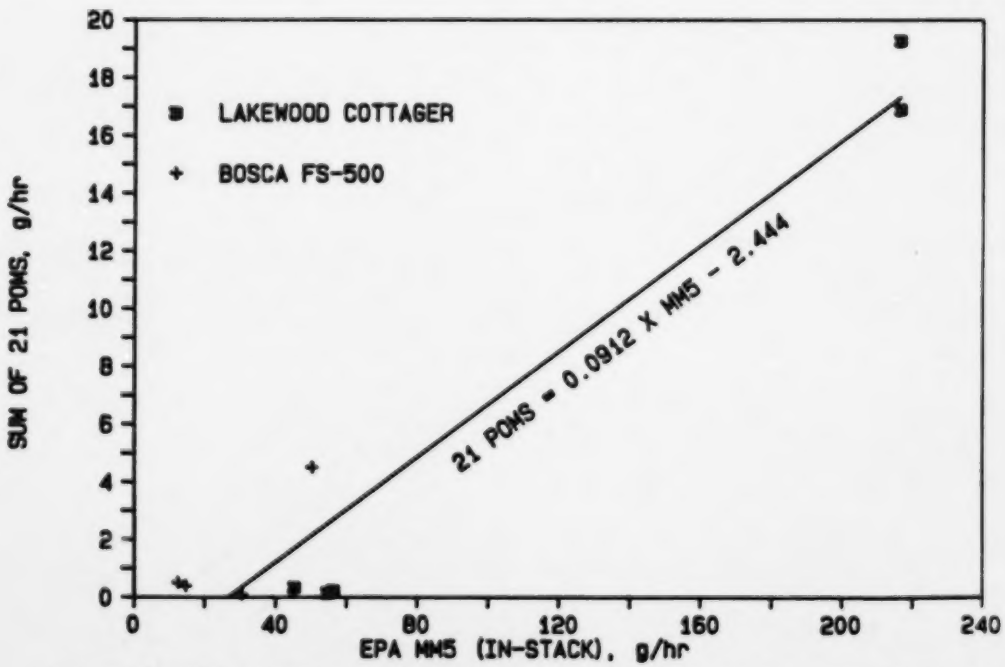

Figure 8. Wood stove emission measurement methods comparison of sum of 21 POMs vs MM5 in-stack in grams per hour for noncatalytic stoves.